The Reaction of Uranyl Ion with Xanthates and Diethyldithiocarbamate

BY RALPH A. ZINGARO[1]

In the presence of potassium ion, some xanthates and diethyldithiocarbamate have been found to form precipitates corresponding to the formula KUO_2X_3, where X is the xanthate or diethyldithiocarbamate radical. On the basis of spectrophotometric data, a double salt structure of the type $UO_2X_2 \cdot K_2UO_2X_4$ is indicated for the diethyldithiocarbamate complex.

Introduction

The preparation of a number of normal uranyl xanthates and dithiocarbamates of the general type UO_2X_2 has been reported by Malatesta,[2] who was able to obtain the xanthates only as impure compounds but prepared the dithiocarbamates as pure solids. The yellow to red solutions formed by the reaction of dithiocarbamates with uranium has led to the use of this type of reagent for the colorimetric determination of uranium.[3,4] During the course of this investigation, which was undertaken during a study of chemical separation methods for uranium, it was found that in the presence of potassium ion, instead of obtaining the normal xanthate or dithiocarbamate, precipitates containing potassium and having a U to S ratio of 1 to 6 were formed. Although these compounds appear to correspond structurally to the type $M(UO_2A_3)$, where A may be acetate, carbonate or oxalate,[5] no evidence was found for the formation of a tris-complex. These compounds were obtained only with potassium ion and for two xanthates among those tested. The diethyl compound was the only one investigated in the dithiocarbamate series.

Experimental

Reagents.—The xanthates were supplied by the American Cyanamid Company. All were recrystallized several times from ligroin–ethanol mixtures before use. The sodium diethyldithiocarbamate was Eastman Kodak Company white label grade and was used without further purification.

The uranyl sulfate and all other salts used were C.P. grade. Uranyl nitrate was prepared at ORNL and contained 48.39% uranium. Analysis after storage over sulfuric acid corresponded to the stoichiometrically pure dihydrate.

All solvents were C.P. grade and were not further purified.

Solutions.—Solutions down to 10^{-3} M were prepared by dissolving weighed amounts of the appropriate salt and diluting with a known amount of solvent at 25°. Lower concentrations were prepared by diluting the stock solutions. Because of the instability of the dithio compounds, all optical measurements were made within 10 minutes of the mixing of the solutions,[6] although all samples were allowed

to stand at least 5 minutes before measurements were made.

All measurements in water were carried out at unit ionic strength adjusted by the addition of sufficient sodium perchlorate. In each case the blank was identical in composition with the sample except for the absence of the complexing agent. A correction for absorption due to equal concentrations of free complexing agent was calculated from measurements made on these substances independently. Although the correction was negligible in the case of the dithiocarbamate, it was appreciable in the case of the ethylxanthate.

Apparatus.—A Cary recording spectrophotometer, Model 11, was used for scanning the over-all spectra. After the absorption curves had been determined, a Beckman Model DU was used for all other measurements.

Analyses.—Uranium was determined by treating a weighed sample with sulfuric and nitric acids, fuming and then diluting. The resulting solution was assayed according to the method of Kolthoff and Lingane,[7] using potassium dichromate as the oxidizing agent and diphenylaminesulfonate as the indicator.

Sulfur was oxidized to sulfate and weighed as barium sulfate.

Potassium was determined gravimetrically,[8] as the sulfate, by digesting a weighed sample with nitric and sulfuric acids, fuming and evaporating to dryness. The residue was redissolved. Uranium was precipitated with ammonia, the combined filtrates were evaporated to dryness in a platinum vessel, and after careful fuming to remove the ammonium sulfate, the residue was weighed as potassium sulfate.

Preparation of the Complexes: $KUO_2(S_2COC_2H_5)_3$.— To a solution containing 4.2 g. (0.01 mole) of uranyl sulfate trihydrate in 150 ml. of water, there was added with stirring, a solution containing 5.0 g. (slightly in excess of 0.03 mole) of potassium ethylxanthate in 50 ml. of water. A brick red precipitate formed rapidly which was filtered off and washed lightly with distilled water. The precipitate was dried *in vacuo* over sulfuric acid. *Anal.* Calcd. for $KUC_9H_{15}O_5S_6$: K, 5.81; U, 35.4; S, 28.6. Found: K, 5.75; U, 35.5; S, 28.8.

$KUO_2[S_2COCH(CH_3)_2]_3$.—A solution containing 12.6 g. (0.07 mole) of sodium isopropylxanthate in 75 ml. of water was saturated with potassium nitrate. To the solution was added rapidly, with stirring, 150 ml. of 0.1 M uranyl sulfate. The red precipitate which formed was filtered off, washed lightly with distilled water and dried *in vacuo* over sulfuric acid. *Anal.* Calcd. for $KUC_{12}H_{21}O_5S_6$: K, 5.47; U, 33.3; S, 26.9. Found: K, 5.54; U, 33.4; S, 27.0.

$KUO_2[S_2CN(C_2H_5)_2]_3 \cdot H_2O$.—To a solution containing 10.2 g. (0.06 mole) of sodium diethyldithiocarbamate and 10 g. of potassium nitrate in 200 ml. of water was added, with stirring, 190 ml. of 0.1 M uranyl sulfate solution. An orange precipitate formed immediately which turned red after a few minutes of stirring. The product, after being filtered and washed with water, was obtained as a pasty red mass. This was dried *in vacuo* over sulfuric acid for at

(1) Permanent address, Chemistry Department, A. and M. College of Texas, College Station, Texas. This work was initiated by the author at the Raw Materials Development Laboratory, Atomic Energy Commission, Winchester, Mass., then operated by the American Cyanamid Company. It was completed while the author was a research participant sponsored by the Oak Ridge Institute of Nuclear Studies.

(2) L. Malatesta, *Gazz. chim. ital.*, **69**, 408 (1939); **69**, 752 (1939).

(3) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1950, p. 603.

(4) C. J. Rodden, "Analytical Chemistry of the Manhattan Project," McGraw–Hill Book Co., Inc., New York, N. Y., 1950, p. 113.

(5) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, New York, N. Y., 1950, p. 1078.

(6) Studies by a number of other workers on the analytical determination of uranium have shown that solutions containing these reagents are stable for a period of two hours without the formation of

colloidal sulfur or change in optical density, and that they obey Beer's law. Reference is made to the work of A. G. Jones and E. F. Orlemann, ORNL Report C-4.360.9, Sept. 7, 1945; C. D. Rothenberger, W. R. Grimes, E. E. Sinclair, and C. C. Casto, ORNL Report C-4.100.21, Oct. 6, 1945; S. Wiberley, C. F. Coleman, M. Korach, E. E. Sinclair, and C. C. Casto, ORNL Report C-4.100.22, Nov. 3, 1945.

(7) I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **55**, 1871 (1933).

(8) I should like to acknowledge the assistance of Mr. Ray Broisman of the American Cyanamid Company, who performed the potassium analyses.

least 24 hr. and reached constant composition, apparently as the monohydrate. *Anal.* Calcd. for $KUC_{15}H_{32}O_3N_3$: K, 5.06; U, 30.8; S, 24.9. Found: K, 5.10; U, 30.8; S, 25.0.

Results of Experiments

The three complexes prepared were all readily soluble in polar organic solvents such as alcohols, ethers and ketones. The dithiocarbamate was very soluble in chloroform, but the xanthates were found to be completely insoluble in this solvent. None dissolved in benzene and the water solubility was very slight in every case. All of these compounds exhibited visible decomposition after a week of storage in a desiccator, and considerable decomposition was observed after two weeks. The breakdown of these compounds was accelerated by moisture. All solutions showed the deposition of colloidal sulfur after standing a few hours. The thermal stability is very limited; visible decomposition began at 35°.

Among other xanthates which were tested were the *n*-propyl, *n*-butyl, isobutyl, *n*-amyl and iso-amyl derivatives. No similar complexes were formed with any of these; only impure products, which decomposed rapidly, were obtained. It will be noted from the Experimental part that a large excess of the potassium ion was necessary for the preparation of some of the complexes. When, instead of potassium, large concentrations of other cations such as ammonium, lithium, sodium, magnesium, calcium, strontium and barium were used, formation of similar compounds in which these metals replaced potassium did not occur. In the presence of iron, copper, vanadium and other heavy metals, either the xanthates or unstable sulfur-bearing precipitates of these metals were formed.

The spectrum[9] of the diethyldithiocarbamate complex exhibited a gradual increase in optical density which leveled off to a broad maximum in the vicinity of 380 mμ and then rose very steeply as the wave length decreased beyond 360 mμ. The spectrum was identical in solvents of widely different polarities. The extinction coefficient at 380 mμ was 4170 in chloroform, 3940 in ethanol and 4060 in water. The similarity among the spectra and the close agreement among the values for the extinction coefficients in the various solvents suggests that the absorbing species must be the same in each case.

In an effort to identify the complexes, the method of Yoe and Jones[10] was used, but the formation constant of the complex was not sufficiently large to permit the formula of the complex to be determined by this method. The application of Job's method of continuous variations[11] is shown in Fig. 1. The formation of a 1:4 complex is clearly indicated for the uranyl–diethyldithiocarbamate system, whereas a 1:2 complex is formed in the uranyl–ethylxanthate system.

(9) All the spectra referred to in this paper have been deposited as Document number 4808 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm in advance payment by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(10) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

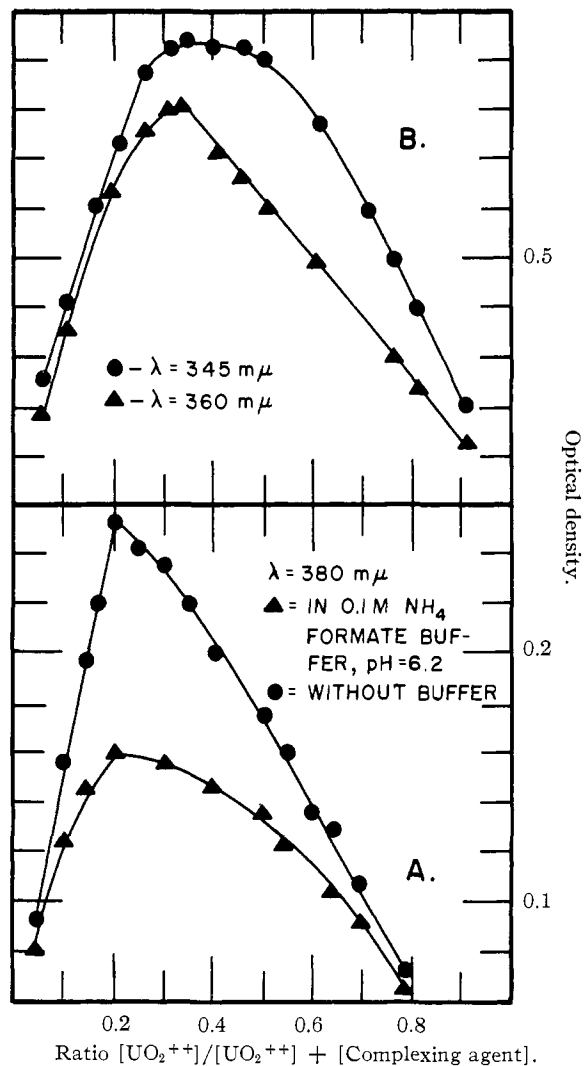(11) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

Fig. 1.—Continuous variation curves: A, lower curves, the system uranyl nitrate–sodium diethyldithiocarbamate in water, total concentration = 4×10^{-4} *M*; B, upper curves, the system uranyl nitrate–potassium ethylxanthate in ethanol, total concentration = 1.6×10^{-3} *M*.

The solubility of the solid diethyldithiocarbamate complex in chloroform and its very slight solubility in water is indicative of strong, covalent grouping with a symmetrical distribution of the non-polar groups. Since only very slight, if any, dissociation can be expected upon dissolution in chloroform, the molecular structure should not be largely distorted in this medium. The presence of the tetrakis-(diethyldithiocarbamato)-uranate(VI) ion is indicated from the spectral data. The stoichiometry requires a sulfur to uranyl to potassium ratio of 6 to 1 to 1. These requirements would be satisfied by a double salt structure of the type $UO_2X_2 \cdot K_2UO_2X_4$, where X is the diethyldithiocarbamate radical. The formation of the normal salt[2] would be expected under the preparative condition described. Both uranium ions in such a structure would exhibit a coördination number of six, the dithiocarbamate acting as a bidentate group around one uranyl ion and as a monodentate group around the other.

Calculations of the dissociation constant for the tetrakis-(diethyldithiocarbamato)-uranate(VI) ion were made according to the method of Foley and Anderson,[12] which utilizes solution pairs having the same concentration of the complex but differing in concentrations of the free complex forming ions. Such data were available directly from the Yoe and Jones type of plot, the continuous variation curves, or appropriate dilutions of these solutions in 1 M sodium perchlorate. Calculated values for three solution pairs gave six values ranging from 1.5 × 10^{-18} to 6.9 × 10^{-18} at 25° for the equilibrium defined by the equation

$$K = \frac{[UO_2^{++}][X^-]^4}{[UO_2X_4^{-2}]}$$

where X is diethyldithiocarbamate. The free energy of formation of the complex as calculated from the values of K is about 23 to 25 kcal./mole. The values for the dissociation constants are at best approximations. The hydrolysis of the uranyl ion, which is appreciable at pH values above 3, and the hydrolysis of the dithio acid salt are both neglected as is also equilibrium with other complexes. In the region of low pH, where hydrolysis of uranyl ion does not occur, the dithio acids are decomposed thus precluding any measurements.

The spectrum of the ethylxanthate complex was similar to that of the dithiocarbamate complex except that the maximum occurred in the vicinity of 360 mμ and then rose very steeply as the wave

(12) R. T. Foley and R. C. Anderson, This Journal, **71**, 909 (1949).

length decreased beyond 340 mμ. The complex absorbed much more strongly in ethanol than in water, indicating considerable dissociation in the latter solvent. For this reason the continuous variation curves were run in ethanol. Plotting according to the method of Yoe and Jones gave values for the extinction coefficient in ethanol of 2.5 × 10^3 at 345 mμ and 2.2 × 10^3 at 360 mμ. Similar calculations made for solutions of the solid in alcohol give the values 2.2 × 10^3 at 345 mμ and 1.9 × 10^3 at 360 mμ. The insolubility of the solid complex in non-polar solvents limits the value of the spectral data insofar as obtaining information about the structure of the solid is concerned. The existence of UO_2X_2 in solutions of the solid in ethanol suggests that it may be a double salt of the type $KX\cdot UO_2X_2$, where X is the ethylxanthate group. The data in no way preclude the possibility of the existence of tris- or tetrakis- complexes. No definite conclusions concerning the structure of the solid appear to be justified, on the basis of these data.

Photolysis of Acetone-d_6 in the Presence of n-Butane and of n-Butane-2,2,3,3-d_4. A Study of the Abstraction of Primary and Secondary Hydrogen by Methyl Radicals

By James R. McNesby and Alvin S. Gordon

Mixtures of n-butane-2,2,3,3-d_4 and acetone-d_6 and of n-butane and acetone-d_6 were irradiated with a medium pressure mercury arc. From the analysis of the methanes produced the activation energies for the following reactions were deduced: $CD_3 + CH_3CD_2CD_2CH_3 \rightarrow CD_3H + CH_2CD_2CD_2CH_3$, $E = 11.4$ kcal.; $CD_3 + CH_3CD_2CD_2CH_3 \rightarrow CD_4 + CH_3CDCD_2$-$CH_3$, $E = 11.4$ kcal.; $CD_3 + CH_3CH_2CH_2CH_3 \rightarrow CD_3H + CH_3CHCH_2CH_3$, $E = 9.3$ kcal. In the system acetone-d_6-butane-d_4, it was found that H is abstracted by CH_3 and CD_3 at about the same specific rate. The pre-exponential factors in the Arrhenius equations for abstraction of primary and secondary hydrogen from n-butane are in the ratio 1.5 compared with the statistical ratio of 1.5. In n-butane-d_4 the ratio of pre-exponential factors for abstraction of primary hydrogen and secondary deuterium is 0.92 compared with a statistical ratio of 1.5.

Introduction

The comparison of the relative rates of abstraction of D from acetone-d_6 and H from hydrocarbons by the CD_3 radical has proved a valuable tool for precise measurement of the activation energies of such metathetical reactions. Measurements made upon hydrocarbons containing more than one kind of hydrogen, e.g., butane, cannot be interpreted unambiguously. For this reason we have prepared practically pure $CH_3CD_2CD_2CH_3$ by the photolysis of α,α'-diethyl ketone-d_4[1] and studied the photolysis of acetone-d_6 in its presence.

(1) J. R. McNesby, C. M. Drew and Alvin S. Gordon, *J. Phys. Chem.*, **59**, 988 (1955).

Results and Discussion

1. Acetone-d_6 and n-Butane-2,2,3,3-d_4.—Mixtures of acetone-d_6 and butane-d_4 were photolyzed in the temperature range 356–450°, employing a previously described technique.[2] The advantage of working in this temperature range is that the secondary butyl radical formed upon abstraction of D from butane-d_4 is thermally unstable and decomposes to give propylene and a light methyl radical. It has therefore been possible to compare the relative rates of abstraction of H and D by the CH_3 radical, as well as by the CD_3 radical, in the

(2) J. R. McNesby and Alvin S. Gordon, This Journal, **76**, 4196 (1954).